

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 421 609 A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90309728.5

(51) Int. Cl.⁵: C09D 133/06, C09D 151/06

(22) Date of filing: 05.09.90

(30) Priority: 05.09.89 US 402293

(43) Date of publication of application:
10.04.91 Bulletin 91/15(84) Designated Contracting States:
BE DE ES FR GB IT(88) Date of deferred publication of the search report:
12.02.92 Bulletin 92/07

(71) Applicant: E.I. DU PONT DE NEMOURS AND
COMPANY
1007 Market Street
Wilmington Delaware 19898(US)

(72) Inventor: Denhartog, Herman Charles
460 Shellbourne
Rochester, Michigan 48309(US)
Inventor: Konsza, Eileen E.
RD. No. 2, Box 307, Colony Court,
Swedesboro
New Jersey, 08085(US)
Inventor: Matthews, James F.
16 Marigold Circle
Levittown, Pennsylvania 19054(US)
Inventor: Werner, Ervin Robert, Jr.
33 Hunt Road
Levittown, Pennsylvania, 19056(US)

(74) Representative: Woodcraft, David Charles et
al
BROOKES & MARTIN High Holborn House
52/54 High Holborn
London, WC1V 6SE(GB)

(54) Waterbased acrylic coating composition.

(57) A waterbased coating composition containing about 10-30% by weight of film forming binder dispersed in an aqueous carrier; wherein the binder contains about

a. 60-90% by weight, based on the weight of the binder, of a methylol (meth)acrylamide acrylic polymer of polymerized monomers of alkyl methacrylate, alkyl acrylate or mixtures thereof, 1-10% by weight, based on the weight of the acrylic polymer, of methylol methacrylamide, methylol acrylamide or mixtures thereof, 0.5-10% by weight, based on the weight of the acrylic polymer, of an ethylenically unsaturated carboxylic acid, 0.5-10% by weight, based on the weight of the acrylic polymer, of an ethylenically unsaturated hydroxyl containing monomer and the acrylic polymer has a glass transition

temperature of -40 to +40C and a weight average molecular weight of 500,000 to 3,000,000; and the carboxyl groups of the carboxylic acid are reacted with ammonia to provide a pH to the composition of about 7.0-10.0;

b. 10-40% by weight, based on the weight of the binder, of a polyurethane which is either a polyester urethane, polyether urethane or polyacrylourethane; the composition forms an automotive quality clear coat and/or pigmented color coat for automobiles and trucks; and the acrylic polymer can be used to form an automotive quality primer composition.

EP 0 421 609 A3



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 9728

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)		
Y	EP-A-0 195 931 (VIANOVA KUNSTHARZ AKTIENGESELLSCHAFT) * page 6, line 22 - page 7, line 29; claims *** page 10, line 1 - line 19 ** - - -	1-5,9-15, 18-22	C 09 D 133/06 C 09 D 151/06		
D	EP-A-0 195 931 (& US-A-4 730 020) - - -				
Y	EP-A-0 089 497 (BASF FARBEN + FASERN AKTIENGESELLSCHAFT) * whole document* * - - -	1-5,9-15, 18-22			
D	EP-A-0 089 497 (& US-A-4 489 135) - - -				
A	US-A-4 451 597 (CLAUS VICTORIUS) * column 4, line 20 - column 5, line 21; claims 1,2,14-19 *** column 6, line 1 - line 52 *** column 7, line 17 - line 18 *** column 8, line 3 - line 54 ** - - -	1-5,19-26			
A	FR-A-2 083 108 (FARBENFABRIK BAYER AKTIENGESELLSCHAFT) * page 4, line 13 - line 29; claims 1,2 *** page 6, line 34 - page 7, line 19 *** page 10, line 20 - page 11, line 3 ** - - -	1-5,10, 11,13,22	TECHNICAL FIELDS SEARCHED (Int. Cl.5)		
A	GB-A-2 060 654 (KANSAI PAINT CO. LTD.) * whole document* * - - - - -	1,6,7	C 09 D		
The present search report has been drawn up for all claims					
Place of search The Hague		Date of completion of search 03 December 91	Examiner PAMIES OLLE S.		
<table><tr><td>CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention</td><td>Legend E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</td></tr></table>				CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention	Legend E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention	Legend E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document				



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 421 609 A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90309728.5

(51) Int. Cl.⁵: **C09D 133/06**, **C09D 151/06**,
/(C09D133/06,175:04),
(C09D151/06,175:04)

(22) Date of filing: 05.09.90

The title of the invention has been amended
(Guidelines for Examination in the EPO, A-III,
7.3).

(30) Priority: 05.09.89 US 402293

(43) Date of publication of application:
10.04.91 Bulletin 91/15

(84) Designated Contracting States:
BE DE ES FR GB IT

(71) Applicant: **E.I. DU PONT DE NEMOURS AND
COMPANY**
1007 Market Street
Wilmington Delaware 19898(US)

(72) Inventor: **Denhartog, Herman Charles**
460 Shellbourne

Rochester, Michigan 48309(US)
Inventor: **Konsza, Eileen E.**
RD. No. 2, Box 307, Colony Court,
Swedesboro
New Jersey, 08085(US)
Inventor: **Matthews, James F.**
16 Marigold Circle
Levittown, Pennsylvania 19054(US)
Inventor: **Werner, Ervin Robert, Jr.**
33 Hunt Road
Levittown, Pennsylvania, 19056(US)

(74) Representative: **Woodcraft, David Charles et
al**
BROOKES & MARTIN High Holborn House
52/54 High Holborn
London, WC1V 6SE(GB)

(54) **Waterbased acrylic coating composition.**

(57) A waterbased coating composition containing about 10-30% by weight of film forming binder dispersed in an aqueous carrier; wherein the binder contains about

a. 60-90% by weight, based on the weight of the binder, of a methylol (meth)acrylamide acrylic polymer of polymerized monomers of alkyl methacrylate, alkyl acrylate or mixtures thereof, 1-10% by weight, based on the weight of the acrylic polymer, of methylol methacrylamide, methylol acrylamide or mixtures thereof, 0.5-10% by weight, based on the weight of the acrylic polymer, of an ethylenically unsaturated carboxylic acid, 0.5-10% by weight, based on the weight of the acrylic polymer, of an ethylenically unsaturated hydroxyl containing monomer and the acrylic polymer has a glass transition temperature of -40 to +40°C and a weight average molecular weight of 500,000 to 3,000,000; and the carboxyl groups of the carboxylic acid are reacted with ammonia to provide a pH to the composition of about 7.0-10.0;

b. 10-40% by weight, based on the weight of the binder, of a polyurethane which is either a polyester urethane, polyether urethane or polyacrylourethane;

the composition forms an automotive quality clear coat and/or pigmented color coat for automobiles and trucks; and the acrylic polymer can be used to form an automotive quality primer composition.

EP 0 421 609 A2

WATERBASED METHYLOL (METH)ACRYLAMIDE ACRYLIC POLYMER AND POLYURETHANE CONTAINING COATING COMPOSITION

BACKGROUND OF THE INVENTION

This invention is directed to a waterbased coating composition and in particular to a waterbased coating
5 containing an methylol (meth)acrylamide acrylic polymer and a polyurethane.

Methylol (meth)acrylamide acrylic polymers are polymers containing polymerized monomers of methylol methacrylamide or methylol acrylamide or any mixtures thereof.

Water based coating compositions useful for base coats and clear coats for automotive applications are shown in Wilfinger et al US 4,730,020, issued March 8, 1988. Waterbased dispersions of polyurethane are
10 known as shown in Drexler et al US 4,489,135, issued December 15, 1984. Processes for preparing aqueous dispersions of acrylic polyesters are shown in Osborn et al US 3,925,295 issued December 9, 1975 and Osmond et al US 3,935,155 issued January 27, 1976. However, none of the compositions shown in the art form finishes having properties that are required in particular for finishing or repair of exterior finishes of automobiles and trucks.

To date, solvent based finishes have been used to repair and refinish the exterior of automobiles and
15 trucks. Finishes of these solvent based compositions provided the required color match, cured at ambient temperatures, had excellent adhesion to the substrate and gave properties such as gloss, hardness, distinctness of image required for the exterior of automobiles and trucks. To reduce solvent emissions, waterbased paints were suggested for use. However, none of the known water based paints form finishes
20 that have the necessary properties for automotive and truck use.

Waterbased color coat for color coat/clear coat finish, i.e., a finish having a pigmented colored layer and a top clear layer, for automobiles and trucks now is coming into use for the manufacturing of original equipment. To repair such a finish, it would be very desirable and usually necessary to use a waterbased finish to match the original color particularly when metallic flake pigments are present in the color coat.

25

SUMMARY OF THE INVENTION

30 A waterbased coating composition containing about 10-30% by weight of film forming binder dispersed in an aqueous carrier; wherein the binder contains about

a. 60-90% by weight, based on the weight of the binder, of a methylol (meth)acrylamide acrylic polymer of polymerized monomers of alkyl methacrylate, alkyl acrylate or mixtures thereof, 1-10% by weight,
35 based on the weight of the acrylic polymer, of methylol methacrylamide, methylol acrylamide or mixtures thereof, 0.5-10% by weight, based on the weight of the acrylic polymer, of an ethylenically unsaturated carboxylic acid, 0.5-10% by weight, based on the weight of the acrylic polymer, of an ethylenically unsaturated hydroxyl containing monomer and the acrylic polymer has a glass transition temperature of -40 to +40C and a weight average molecular weight of 500,000 to 3,000,000, the carboxyl groups of the carboxylic acid are reacted with ammonia to provide a pH of about 7.0-10.0; and

40 b. 10-40% by weight, based on the weight of the binder, of a polyurethane which is either a polyester urethane, polyether urethane or polyacrylourethane; the composition forms an automotive quality clear coat and/or pigmented color coat for automobiles and trucks; and the acrylic polymer can be used to form an automotive quality primer composition.

45

DETAILED DESCRIPTION OF THE INVENTION

50 The coating composition of the invention is stable for extended periods of time, has a very low VOC (volatile organic content), can be pigmented with all existing commercial pigments used for automobiles and trucks, forms finishes that are hard, glossy, weatherable and durable. In particular, the composition has excellent adhesion to a variety of substrates such as previously painted substrates, cold rolled steel, phosphatized steel, steel coated with conventional primers such as electrodeposition primers that typically are crosslinked epoxy polyesters and various epoxy resin, alkyd resin repair primers, plastic substrates

such as polyester reinforced fiber glass, reaction injection molded urethanes and partially crystalline polyamides. A clear coat can be applied to a layer of the pigmented composition to provide a clear/color coat finish. The coating composition used for the clear coat can be the coating composition of this invention or another compatible aqueous or solvent based coating composition.

5 The coating composition either with or without the polyurethane constituent can be used as a primer over cold rolled steel, treated steel such as phosphatized steel or the aforementioned plastic substrates. The primer provides a surface to which a topcoat will adhere such as a topcoat of the coating composition of this invention as described above.

The coating composition has a film forming binder content of about 10-30% by weight and correspond-
10 ingly, about 90-70% by weight of an aqueous carrier which is primarily water but often contains small amounts of organic solvents for the binder. The composition may be used as a clear coating composition which may contain very small amounts of pigment to eliminate color such as yellowing. Generally, the composition is pigmented and contains pigments in a pigment to binder weight ratio of about 1:100 - 200:100.

15 The film forming binder of the composition contains about 60-90% by weight of the methylol (meth)-acryamide acrylic polymer and correspondingly about 10-40% by weight of a polyurethane. Preferably, the binder contains about 65-85% by weight of the acrylic polymer and 35-15% by weight of the polyurethane. Preferably, for solid color compositions, i.e. compositions in which metallic pigments such as aluminum flake are not used, the binder contains about 70% acrylic polymer and 30% polyurethane and for metallic
20 colors, i.e. compositions containing aluminum flake, the binder contains about 80% acrylic polymer and 20% polyurethane.

The acrylic polymer is formed by conventional emulsion polymerization by emulsifying a mixture of monomers, water, surfactant and polymerization catalyst and charging the resulting emulsion into a
25 conventional polymerization reactor and heating the constituents in the reactor to about 60-95C for about 15 minutes to 8 hours and then the resulting polymer is neutralized with ammonia or an amine. The size of the polymeric particles of the latex is about 0.06-0.20 microns. The resulting polymer has a hydroxyl no. of 2-100, a glass transition temperature of -40 to +40C and a weight average molecular weight of about 500,000 - 3,000,000.

All molecular weights herein are measured by gel permeation chromatography using polystyrene as the
30 standard.

Typically useful catalysts are ammonium persulfate, hydrogen peroxide, sodium meta bisulfite, hydrogen peroxide sodium sulfoxylate and the like.

Typically useful surfactants are nonylphenoxypolyethyleneoxy ethanol sulfate, allyl dodecyl sulfosuccinate, alkyl phenoxy polyethylene oxyethanol, sodium lauryl sulfate and mixtures thereof. One preferred
35 surfactant is a mixture of nonylphenoxy polyethyleneoxy ethanol sulfate and allyl dodecyl sulfosuccinate.

The acrylic polymer contains about 1-10% by weight of polymerized methylol methacrylamide, methylol acrylamide or any mixtures thereof.

The acrylic polymer preferably contains sufficient polymerized hydroxy alkyl methacrylate or acrylate having 2-4 carbon atoms in the alkyl group to provide the polymer with a hydroxyl no. of 2-100. Usually,
40 about 2-10% by weight of hydroxy alkyl acrylate or methacrylate is used. Typically useful monomers are hydroxyethyl acrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate. Other useful polymerizable constituents are reaction products of an alkyl methacrylate or acrylate and a lactone. A constituent of this type is "Tone" 100 made by Union Carbide which is believed to be the reaction product of hydroxyethyl acrylate and a lactone.

45 The acrylic polymer also contains sufficient polymerized monoethylenically unsaturated acid monomers. Typically useful monoethylenically unsaturated acids are methacrylic acid, acrylic acid, itaconic acid, styrene sulfonic acid and salts thereof. Usually, these unsaturated acids are used in an amount of about 0.1-10% by weight, based on the weight of the polymer.

The remaining constituents of the acrylic polymer are polymerized alkyl acrylates and/or methacrylates
50 preferably having about 1-12 carbon atoms in the alkyl group. These constituents are blended to provide the desired polymer glass transition temperature. Typically useful monomers are methyl methacrylate, ethyl acrylate, propyl acrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, butyl acrylate, isobutyl acrylate, hexyl acrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, 2-ethylhexyl acrylate, lauryl methacrylate and the like. Also, up to about 20% by weight of styrene can be used to form the acrylic
55 polymer.

The acrylic polymer can contain about 0.1-5% by weight of carbodiimides or polyfunctional aziridines which provide the polymer with additional crosslinking sites. Typically useful carbodiimides have the following structural formula:



where R_1 and R_2 are alkyl groups containing 1-8 carbon groups. One particularly useful carbodiimide is "UCARLNK" Crosslinker XL-25SE made by Union Carbide Corporation.

Useful polyfunctional aziridines include trimethylolpropane-tris-[B-(N-aziridinyl)propionate],
 5 pentaerythritol-tris-[B-(N-aziridinyl)propionate].

The following are particularly useful acrylic polymers:

an acrylic polymer containing about 30-40% by weight methyl methacrylate, 10-20% by weight styrene, 35-45% by weight 2-ethylhexyl acrylate, 1-6% by weight methylol methacrylamide, 1-5% by weight hydroxyethyl acrylate and 1-5% by weight methacrylic acid;

10 an acrylic polymer containing about 25-35% by weight methyl methacrylate, 10-20% by weight styrene, 45-55% by weight 2-ethylhexyl acrylate, 1-6% by weight methylol methacrylamide, 1-5% by weight hydroxyethyl acrylate and 1-5% by weight methacrylic acid;

an acrylic graft copolymer of stage I of 10-30% by weight of methyl methacrylate, 1-5% by weight methylol methacrylamide, 70-89% by weight butyl acrylate grafted to stage II of 70-80% by weight of butyl acrylate,
 15 5-15% by weight methylol methacrylamide, 5-15% by weight hydroxyethyl acrylate and 5-9% by weight methacrylic acid.

a three stage acrylic graft copolymer polymer, wherein stage I and stage II each comprise methyl methacrylate and butyl acrylate, and stage III comprises methyl methacrylate, butyl acrylate and methylol methacrylamide.

20 Typical polyurethanes that are used in the coating composition are in the form of an aqueous dispersion and have a particle size of less than 0.1 microns. These polyurethanes are formed by reacting a polyester, polyether, polycarbonate, polylactone or polyacrylate having terminal hydroxyl groups with a diisocyanate in a molar ratio such that the resulting intermediate product has terminal isocyanate groups. Then the isocyanate groups of this intermediate product are reacted with a compound which has a group that is
 25 reactive with the isocyanate groups and has at least one group that is capable of forming an anion. This group is subsequently neutralized with a tertiary amine to form a water dispersible polyurethane and the resulting polyurethane is then chain extended in water with a diamine by reaction of the diamine with unreacted isocyanate groups of the polyurethane. A process for making such polyurethanes in aqueous dispersion is disclosed in Drexler et al U.S. Patent 4,489,135 issued Dec. 18, 1984 which is hereby
 30 incorporated by reference.

Typical polyester urethanes are formed by preparing a polyester polyol from a polyol and a dicarboxylic acid or an anhydride. Useful acids include succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, maleic acid and anhydrides of these acids. Useful diols include
 35 ethylene glycol, butylene glycol, neopentyl glycol, hexane diol or mixtures of any of the above. The polyester polyol is reacted with suitable diisocyanate in a molar ratio of polyol to diisocyanate of about 1:2 to form an isocyanate terminated product.

Diisocyanates that can be used are as follows: toluene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, ethylethylene diisocyanate, 2,3-dimethylethylene diisocyanate, 1-methyltrimethylene diisocyanate, 1,3-cyclopentylene diisocyanate, 1,4-cyclohexylene
 40 diisocyanate, 1,3-phenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,5-naphthalene diisocyanate, bis-(4-isocyanatocyclohexyl)methane, 4,4'-diisocyanatodiphenyl ether, tetramethyl xylene diisocyanate and the like.

Compounds that are reactive with the isocyanate groups and have a group capable of forming an anion are as follows: dihydroxypropionic acid, dimethylolpropionic acid, dihydroxysuccinic acid and dihydroxybenzoic acid. Other suitable compounds are the polyhydroxy acids which can be prepared by oxidizing
 45 monosaccharides, for example gluconic acid, saccharic acid, mucic acid, glucuronic acid and the like.

Suitable tertiary amines which are used to neutralize the acid and form an anionic group for water dispersability are trimethylamine, triethylamine, dimethylaniline, diethylaniline, triphenylamine and the like.

Diamines suitable for chain extension of the polyurethane to give N-alkylurea groups are as follows:
 50 ethylenediamine, diaminopropane, hexamethylene diamine, hydrazine, aminoethylethanolamine and the like.

Typical polylactones that can be used to form the polyurethane can be lactones such as caprolactone reacted with a diol. Other useful lactones can be represented by the formula



in which n is preferably 4 to 6 and Z is hydrogen, an alkyl radical, a cycloalkyl radical or an alkoxy radical and does not contain more than 12 carbon atoms. The most preferred lactone is epsilon caprolactone since it is readily available and provides a coating with excellent properties. Typically useful aliphatic diols that can be used to form the polylactone are ethylene glycol, 1,3-propanediol, 1,4-butanediol, and dimethylolcyclohexane. Polycaprolactone glycol is another useful constituent.

Typical polyethers that can be used to form the polyurethane are polypropylene glycols having a weight average molecular weight of about 400-4500. Typical polypropylene glycols that can be used are those designated as "Niax" polypropylene glycols 425, 2025, 3025, 4025 and the like. The numbers designate the molecular weight of the polypropylene glycols.

One useful polyester urethane is the reaction product of isophorone diisocyanate, polycaprolactone glycol, trimethylol propane, a polyester of 3-methyl-1,5-pentane diol and adipic acid, dimethylolpropionic acid and is neutralized with triethylamine and has a number average molecular weight of 20,000-30,000.

Typical hydroxyl terminated polyacrylates that can be used to form the polyurethane are prepared by ethylenic polymerization of acrylic esters such as the aforementioned alkyl acrylate or methacrylates with ethylenic unsaturated monomers containing functional groups such as carboxyl, hydroxyl, cyano groups and/or glycidyl groups. Any of the aforementioned alkyl acrylates and methacrylates can be used. Typically useful functional monomers are acrylic acid, methacrylic acid, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, any of the other aforementioned hydroxyalkyl acrylates or methacrylates, glycidyl methacrylate or acrylate, 2-cyanoethyl acrylate or methacrylate and the like.

These polylactones, polyethers or polyacrylates are reacted as shown above for the polyester to form an aqueous polyurethane dispersion.

Typical pigments that can be used in the composition are metallic oxides such as titanium dioxide, zinc oxide, iron oxides of various colors, carbon black, filler pigments such as talc, china clay, barytes, carbonates, silicates, and a wide variety of organic colored pigments such as quinacridones, copper phthalocyanines perylenes, azo pigments, indanthrone blues, carbazoles such as carbazole violet, isoin-dolinones, isindolinones, thioindigo reds, benzimidazolinones and the like.

When the coating contains metallic pigments, agents which inhibit the reaction of the pigments with water may be added. Typical inhibitors are phosphated organic materials such as "Vircopet" 40 available from Mobil Chemical Co.

The pigments can be introduced into the coating composition by first forming a mill base or pigment dispersion with either the methylol (meth)acrylamide acrylic polymer or the polyurethane or with another compatible polymer or dispersant by conventional techniques such as high speed mixing, sand grinding, ball milling, attritor grinding or two roll milling. The mill base is blended with other constituents used in the composition.

The coating composition can contain about 0.01-2% by weight, based on the weight of the binder, of ultraviolet light stabilizers which includes ultraviolet light absorbers, screeners and quenchers. Typical ultraviolet light stabilizers include benzophenones, triazines, triazols, benzoates, hindered amines and blends thereof.

Thickeners and rheology control agents can be added to the coating composition in amounts of about 0.5-5% by weight of the coating composition to provide the desired spray viscosity. Typically, acrylic polymers such as polyacrylic acid, clays such as "Bentones", cellulose, polysaccharides, urethanes or mixtures thereof can be added.

With relatively high glass transition temperature methylol (meth)acrylamide acrylic polymers, i.e. polymers having a glass transition temperature of about 10-40°C, it is preferred to use up to about 10% by weight, based on the weight of the coating composition, of a coalescing solvent. Typical coalescing solvents that can be used are dibasic acid esters, glycol ethers such as propylene glycol ether and ethylene glycol ether and mixtures thereof.

The coating composition can be applied to a plastic or metal substrate by conventional techniques such as spraying, electrostatic spraying, dipping, brushing, flowcoating and the like. The preferred method is spraying. After application, the composition is dried at ambient temperatures but can be baked at about 50-80°C for about 5-45 minutes to form a coating layer about 0.1-2.0 mils thick. Generally the layer is about 0.5-1.5 mils thick. For clear coat/color coat systems a clear layer which can either be a solvent based aqueous based composition is applied over the pigment color coat and baked or dried at ambient temperatures to form a dry film having a thickness of about 1.5-2.5 mils. Aqueous based clear coating compositions of this invention can be used. Acrylic silane aqueous or solvent based compositions can be used as the clear layer.

If the coating composition of this invention is used as a clear layer, it is preferred to use an acrylic polymer in the composition that contains about 0.1-5% by weight of one of the aforementioned car-

bodiimide or aziridiny crosslinkers.

The methylol (meth)acrylamide acrylic polymer can be used to form a primer composition without the presence of the polyurethane. One preferred acrylic polymer useful for primers contains about 35% methyl methacrylate, 15% styrene, 39% 2-ethylhexyl acrylate, 3% methylol methacrylamide, 3% 2-hydroxy ethyl acrylate and 3% methacrylic acid. Typical primer pigments are used in a pigment to binder ratio of about 150:100 to 200:100. The primer composition can be applied to all of the aforementioned substrates using the above application techniques. Preferably, the primer is applied by spraying. The primer can be baked at about 20-135C for about 20-60 minutes to form a dry film about 0.5-3.0 mils thick. The primer has excellent adhesion to metals and previously painted metal substrates.

The following example illustrates the invention. All parts and percentages are on a weight basis unless otherwise indicated. Molecular weights are determined by gel permeation chromatography using polystyrene as the standard.

EXAMPLE 1

A coating composition is prepared by first forming an methylol (meth)acrylamide acrylic polymer latex and then mixing the latex with the other components used in the coating composition.

20

Latex A	Parts By Weight
<u>Portion 1</u>	
Deionized water Nonylphenoxy polyethyleneoxy ethyl sulfate (4 moles EO) Allyl dodecyl sulfosuccinate sodium salt	1318.0 5.0 7.0
<u>Portion 2</u>	
Deionized water Ammonium persulfate	40.0 4.0
<u>Portion 3</u>	
Methyl methacrylate monomer (MMA) Styrene monomer (S) 2-Ethyl hexyl acrylate (2-EHA) N-methylol methacrylamide (MOLMAN) Methacrylic acid monomer (MAA) Nonylphenoxy polyethyleneoxy ethyl sulfate Allyl dodecyl sulfosuccinate sodium salt Deionized water	576.0 240.0 640.0 87.0 48.0 14.0 20.0 908.0
<u>Portion 4</u>	
Deionized water Aqueous ammonium hydroxide solution (29% aqueous solution) Methanol[[(2-dihydro-5-methyl-3(2H)-oxazolyl)-1-methylethoxy]methoxy]methoxy]	30.0 45.0 4.0
Total	4030.0

50

Portion 1 was added to a reaction vessel equipped with a heating mantle, stirrer, thermometer, reflux condenser and two addition funnels. The resulting mixture was heated to 85C with mixing. Portion 2 was placed in a vessel attached to an addition funnel. Portion 3 was emulsified with an Eppenbach homogenizer. 5% of the resulting emulsion was added to the reaction vessel and the temperature of the constituents in the vessel was stabilized at 85C. Portion 2 was then added and held for 5 minutes and then the remainder of the portion 3 emulsion was added over a period of 90 min. at a uniform rate. The temperature of the resulting polymerization mixture was maintained at 88-90C during the addition. The polymerization mixture was held at the above temperature for about 1 hour. The polymerization mixture was cooled to 35C and

then Portion 4 was added to neutralize the latex.

The resulting latex polymer had the following composition: MMA/S/2-EHA/MOLMAN/HEA/MAA in a weight ratio of 36/15/40/3/3/3. The polymer had a weight average molecular weight of about 250,000-1,250,000. The latex had a polymer particle size of 0.095 microns, a gallon weight of 8.55 lbs/gal, pH of 8.77, percent weight solids of 38.9 and a percent volume solids 37.2.

A primer Composition was prepared as follows:

A. Millbase preparation:

The following ingredients were premixed and then ground in an attritor:

	Parts by Weight
Deionized water	150.84
Aqueous ammonium hydroxide solution (29% solution)	1.73
"Tamol" 901 (made by Rohm & Hass, ammonium salt of acrylic copolymer dispersant)	0.83
"Igepal" CO-990 (nonyl phenoxy polyethyleneoxy ethanol 99 moles EO)	3.75
Talc pigment	114.90
Aluminum silicate pigment	57.47
Carbon black pigment (Printex U)	0.37
Titanium dioxide pigment	18.90
Anticorrosive pigment (calcium strontium phosphosilicate)	25.54
Zinc phosphate pigment	38.25
Total	412.58

B> Primer preparation:

The following ingredients were added in order with mixing:

	Parts by Weight
Deionized water	62.12
"Igepal"CO-990 (described above)	0.12
"Texanol" (2,2,4 trimethyl 1,3 pentane diol monoisobutyrate)	11.72
Pine Oil	9.38
"Butyl Cellosolve" (ethylene glycol monobutyl ether)	5.86
Methanol	29.30
Mill Base (prepared above)	412.58
Latex A (prepared above)	424.16
Blend 1 (deionized water 11.89, "Butyl Cellosolve" 3.19, aqueous ammonium hydroxide solution -described above 0.86)	15.94
Blend 2 (deionized water 23.57, "Butyl Cellosolve" 3.58, aqueous ammonium hydroxide solution 1.57 and "Acrysol" TT615 -Rohm & Haas acrylic copolymer thickner 4.10)	32.82
Total	1004.00

The resulting primer composition has a solids content of 40%, and a pigment/binder ratio of 150:100. The primer was sprayed onto cold-rolled steel panels and dried at ambient temperatures. The primer

had a dry film thickness of about 1.8-2.2 mils. The panels were then spray-coated with a two component acrylic urethane base coating composition and a two component acrylic urethane clear coating composition and cured at ambient temperatures for 7 days. The resulting basecoat had a dry film thickness of about 0.9 - 1.2 mils and the clear coat had a dry film thickness of about 1.8 - 2.1 mils and had an excellent appearance, ie. good gloss and distinctness of image.

Steel panel spray coated with the primer and dried as above had the following properties:

Dry film build - 1.8-2.2 mils

Adhesion (96 hrs humidity 38C/100% RH) - good Corrosion resistance (240 hrs. salt spray)-Excellent - creep less than 1/8 inch.

Silver Basecoat Composition

15 A. Millbase preparation:

The following ingredients were combined in the order indicated and mixed for 30 minutes:

	Parts by Weight
Ethylene glycol monobutyl ether	5.49
Inhibitor solution (phosphated organic material)	1.61
Aluminum flake paste (65% solids in Mineral spirits)	3.48
Total	10.58

30 B. Basecoat preparation:

Latex B was prepared using the same constituents and polymerization conditions as used to prepare latex A except the following monomer ratios were used: MMA/S/2-EHA/MOLMAN/HEA/MAA in a weight ratio of 27/15/49/3/3/3. Molecular weight, particle size, gallon weight, pH, weight solids and volume solids were about the same as for the above latex A.

The following ingredients were combined in the order indicated with mixing and added to and blended with the above millbase composition:

	Parts by Weight
Deionized Water	50.67
Latex B (described above)	28.50
Polyether urethane latex (Neorez R-970-ICI Resins - 39% solids of aliphatic polyurethane having a particle size of about 0.1 micron)	7.89
Thickener (acrylic copolymer emulsion polyacrylic acid - Acrysol ASE-60-Rohm and Haas Co.)	1.99
Ammonium hydroxide solution (29% aqueous solution)	0.33
Total	100.00

The resulting coating composition had a solids content of 17.91%, and a pigment/binder ratio of 15/100.

The silver basecoat was sprayed onto primed cold-rolled steel panels. The panels were then spray-coated with the clear coating composition of a two component solvent based acrylic/urethane clear and cured at ambient temperatures for 7 days. The resulting basecoat had a dry film thickness of about 0.6 - 0.8 mils and the clearcoat had a dry film thickness of about 2.3 - 2.6 mils.

The coating on the panels had the following properties:
Appearance - excellent

20 Gloss = 100

5

Dry crosshatch and tape adhesion = 10

Humidity resistance (96 hour at 38C/100% rel. humidity):

Crosshatch adhesion 10

Blistering = 10

10 = Rating system 0-10, 10 best, 0 worst.

White Basecoat Composition

15

A. Millbase preparation:

The following ingredients were charged in a model 01 Attritor:

20

	Parts by Weight
<u>Portion 1</u>	
Deionized water	9.86
Acrylic copolymer dispersion (50% solids aqueous dispersion of methyl methacrylate/butyl acrylate/methacrylic acid polymer neutralized with ammonia)	0.81
Titanium dioxide pigment	19.73
<u>Portion 2</u>	
Latex B (described above)	8.83
Total	39.23

35

Portion 1 was ground for about 4.5 hours and then Portion 2 was added and ground for an additional 1.5 hour to form the millbase.

40

B. Basecoat preparation:

The following ingredients were combined in the order indicated with mixing and added to and blended with the above prepared millbase:

45

	Parts by Weight
Deionized Water	20.01
Latex B (prepared above)	23.93
Polyether urethane latex (described above)	15.30
Thickener (described above)	1.04
Ammonium hydroxide solution (29% aqueous solution)	0.37
Total	100.00

55

The resulting coating composition had a solids content of 39.60%, and a pigment/binder ratio of 100:100.

The white basecoat was sprayed onto primed cold-rolled steel panels. The panels were then spray-coated with the clear coating composition 1080S 2K urethane clear described above and cured at ambient temperatures for 7 days. The resulting basecoat had a dry film thickness of about 2.0 mils and the clearcoat had a dry film thickness of about 2.0 mils.

5 The coating on the panels had the following properties:

Appearance - excellent

20° Gloss = 96.4

10 Dry crosshatch and tape adhesion = 10

Humidity resistance (96 hour at 38C/100% rel. humidity):

Crosshatch adhesion = 10

Blistering = 10

Rating system 0-10, 10 best, 0 worst.

15

EXAMPLE 2

20 The following constituents were blended together to form a clear coating composition:

	Parts By Weight
25 Latex B (prepared in Example 1)	256.0
"Butyl Cellosolve" (described in Example 1)	20.0
Aqueous polyurethane dispersion (described below)	62.5
30 Carbodiimide crosslinker ("UCARLNK" crosslinker XL-25SE made by Union Carbide Corporation)	10.0
Total	348.5

35 The above clear coating composition was sprayed onto primed steel panels and dried at ambient temperatures for 7 days. The resulting clear coated panels had excellent clarity, good gloss and distinctness of image, good water spot resistance, good solvent resistance, excellent chip resistance, good corrosion resistance and good room temperature flexibility.

40 The above clear coating composition can be sprayed onto primed steel panels coated with the silver basecoating composition of Example 1 and onto primed steel panels coated with the white basecoating composition of Example 1 and dried as above. It is expected that the resulting clear coated panels will have the same or very similar physical properties as shown above.

A clear coating composition was prepared using the same above constituents except the carbodiimide crosslinker was omitted. The resulting clear coating was sprayed onto primed steel panels and dried as above. The resulting clear coated panels has properties similar to those shown above.

45 The polyurethane of the above dispersion is the reaction product of 30.3 parts by weight of isophorone diisocyanate, 29.2 parts polycaprolactone glycol, 1.6 parts trimethylolpropane, 28.2 parts of a polyester of 3-methyl-1,5-pentane diol and adipic acid 4.7 parts dimethylolpropionic acid and is neutralized with 4.2 parts triethylamine.

50 Claims

1. A waterbased coating composition comprising about 10-30% by weight of film forming binder dispersed in an aqueous carrier; wherein the binder consist essentially of about
 - 55 a. 60-90% by weight, based on the weight of the binder, of an methylol (meth)acrylamide acrylic polymer consisting essentially of polymerized monomers of alkyl methacrylate, alkyl acrylate or mixtures thereof, 1-10% by weight, based on the weight of the acrylic polymer, of methylol methacrylamide, methylol acrylamide or mixtures thereof, 0.5-10% by weight, based on the weight of the acrylic polymer

- of an ethylenically unsaturated carboxylic acid, 0.5-10% by weight, based on the weight of the acrylic polymer, of an ethylenically unsaturated hydroxylcontaining monomer, said acrylic polymer having a glass transition temperature of -40 to +40C and a weight average molecular weight of 500,000 to 3,000,000; and the carboxyl groups of the carboxylic acid are reacted with ammonia or an amine to provide a pH of about 7.0-10;
- 5 b. 10-40% by weight, based on the weight of the binder, of a polyurethane selected from the group consisting of polyester urethane, polyether urethane or polyacrylourethane.
2. The coating composition of claim 1 containing pigment in a pigment to binder weight ratio of about 1:100-200:100.
- 10 3. The coating composition of claim 1 in which the acrylic polymer consists essentially of polymerized monomers of an alkyl methacrylate, an alkyl acrylate or mixtures thereof each having 1-12 carbon atoms in the alkyl group, 2-10% by weight of a hydroxy alkyl methacrylate or acrylate having 2-4 carbon atoms in the alkyl group, 0.1-10% by weight of a monoethylenically unsaturated carboxylic acid and 1-10% by weight of methylol acrylamide, methylol methacrylamide or mixtures thereof.
- 15 4. The coating composition of claim 1 in which the acrylic polymer contains up to 20% by weight of polymerized styrene.
5. The coating composition of claim 4 in which the acrylic polymer consists essentially of about 30-40% by weight methyl methacrylate, 10-20% by weight of styrene, 35-45% by weight of 2-ethylhexyl acrylate, 1-6% by weight methylol methacrylamide, 1-5% by weight of hydroxyethyl acrylate and 1-5% by weight
- 20 methacrylic acid.
6. The coating composition of claim 1 in which the acrylic polymer is a graft copolymer consisting essentially of stage I of 10-30% by weight of methyl methacrylate, 1-5% by weight of methylol methacrylamide and 70-89% by weight butyl acrylate grafted to stage II of 70-80% by weight of butyl acrylate, 5-15% by weight methylol methacrylamide, 5-15% by weight of hydroxyethyl acrylate and 5-9%
- 25 by weight methacrylic acid.
7. The coating composition of claim 1 in which the acrylic polymer is a graft copolymer consisting essentially of stages I, II and III, wherein stages I and II comprise methyl methacrylate, butyl acrylate and stage III comprises methyl methacrylate, butyl acrylate and methylol methacrylamide.
8. The coating composition of claim 1 containing about 0.1-5% by weight, based on the weight of the
- 30 acrylic polymer, of a crosslinking agent of a carbodiimide or a polyfunctional aziridine.
9. The coating composition of claim 1 in which the polyurethane is a polyester urethane.
10. The coating composition of claim 9 in which the polyester urethane consists essentially of polyester polyol of a polyol and a dicarboxylic acid or an anhydride thereof, said polyester polyol is reacted with an organic diisocyanate which in turn is reacted with a hydroxy containing carboxylic acid, said acid being
- 35 neutralized with a tertiary amine and the resulting product chain extended with a diamine.
11. The coating composition of claim 10 in which the polyester urethane consists essentially of a polyester polyol of a lactone reacted with a polyol, said polyester polyol is reacted with an organic diisocyanate which in turn is reacted with a hydroxy containing carboxylic acid, said acid being neutralized with a tertiary amine and the resulting product chain extended with a diamine.
- 40 12. The coating composition of claim 9 in which the polyurethane is the reaction product of isophorone diisocyanate, polycaprolactone polyol, trimethylolpropane, polyester of pentanediol and adipic acid, dimethylolpropionic acid and neutralized with triethylamine.
13. The coating composition of claim 1 in which the polyurethane is a polyether urethane.
14. The coating composition of claim 13 in which the polyether urethane consists of a polyalkylene glycol
- 45 having a weight average molecular weight of about 400-4500, said polyalkylene glycol is reacted with an organic diisocyanate which in turn is reacted with a hydroxy containing carboxylic acid, said acid being neutralized with a tertiary amine and the resulting product chain extended with a diamine.
15. The coating composition of claim 14 in which the polyalkylene glycol consists essentially of polypropylene glycol.
- 50 16. The coating composition of claim 1 in which the polyurethane is a polyacrylourethane.
17. The coating composition of claim 16 in which the polyacrylourethane consists essentially of a functional acrylic polymer of polymerized ethylenically unsaturated acrylic esters and ethylenically unsaturated monomers containing functional groups selected from the group consisting of carboxyl, hydroxyl, cyano, or glycidyl groups, said functional acrylic polymer is reacted with diisocyanate which in turn is reacted with a
- 55 hydroxy containing carboxylic acid, said acid being neutralized with a tertiary amine and the resulting product chain extended with a diamine.
18. The coating composition of claim 1 in which the acrylic polymer consists essentially of polymerized monomers of an alkyl methacrylate, an alkyl acrylate or mixtures thereof each having 1-12 carbon atoms in

the alkyl group, 2-10% by weight of a hydroxy alkyl methacrylate or acrylate having 2-4 carbon atoms in the alkyl group, 0.1-10% by weight of a monoethylenically unsaturated carboxylic acid and 1-10% by weight of methylol acrylamide, methylol methacrylamide or mixtures thereof; and in which the polyurethane is a polyester urethane consisting essentially of a polyester polyol of a polyol and a dicarboxylic acid or an anhydride thereof said polyester polyol is reacted with an organic diisocyanate which in turn is reacted with a hydroxy containing carboxylic acid said acid being neutralized with a tertiary amine and the resulting product chain extended with a diamine.

19. A water based primer composition comprising about 10-30% by weight of a film forming binder dispersed in an aqueous carrier; wherein the binder consists of about acrylic polymer consists essentially of about 30-40% by weight methyl methacrylate, 10-20% by weight of styrene, 35-45% by weight of 2-ethylhexyl acrylate, 1-6% by weight methylol methacrylamide, 1-5% by weight of hydroxyethyl acrylate and 1-5% by weight methacrylic acid;

wherein the acrylic polymer has a glass transition temperature of -40 to +40C and a weight average molecular weight of 500,000 to 3,000,000 and the composition contains pigments in a pigment to binder weight ratio of about 50:100-200:100.

20. A water based coating composition comprising about 10-30% by weight of a film forming binder dispersed in an aqueous carrier; wherein the binder consists of about acrylic polymer consists essentially of about 25-35% by weight methyl methacrylate, 10-20% by weight of styrene, 45-55% by weight of 2-ethylhexyl acrylate, 1-6% by weight methylol methacrylamide, 1-5% by weight of hydroxyethyl acrylate and 1-5% by weight methacrylic acid;

wherein the acrylic polymer has a glass transition temperature of -40 to +40C and a weight average molecular weight of 500,000 to 3,000,000.

21. A substrate coated with a dried and cured layer of the composition of claim 1.

22. The substrate of claim 21 in which the substrate is a metal.

23. The substrate of claim 21 in which the substrate is a plastic.

24. The substrate of claim 21 in which the substrate is a plastic reinforced with fiberglass.

25. A substrate coated with a dried clear layer of the cured composition of Claim 1 in adherence to a pigmented color layer of a coating composition.

26. A substrate coated with a dried pigment color layer of the cured composition of claim 1 and having firmly adhered to the color layer a clear layer of the cured composition of claim 1.